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ABSTRACT

The dissociation energy and the equilibrium bond length are determined for ClO at the first order CI level for a variety of basis sets. These basis sets consisted of both standard atomic centered basis sets and those including bond functions. CI calculations were then performed on the Cl atom using only the Cl atomic centered basis set and the ClO basis sets at the ClO equilibrium bond length. The basis sets with bond function are found to have a CI superposition error many times that of the standard atomic centered basis sets. For a DZP atomic centered basis set augmented with s, p, and d bond function the CI superposition error was as large as 0.408 eV.

Introduction

Peyerimhoff and Buenker[1] (PB) have shown that accurate dissociation energies can be obtained if they use basis sets which contain bond functions with the same maximum ℓ-value as the atomic centered functions. The fact that basis sets as small as double zeta plus s and p bond functions (DZ + Bf(sp)) can be used to compute the dissociation energy of $C\ell O$ with an error of only 2.6 kcal/mole seems to contradict the standard beliefs on the accuracy of basis sets. In fact for N_2 they found this basis set predicted a D_e which was greater than the experimental determination.

The use of bondfunctions leads to some consistency problems in applications involving the investigation of structure. For example in the calculation of the potential energy path between cyclic and linear X_3, the bond functions in the breaking bond would migrate to the central atom in the linear geometry. In addition to the problem of how to choose and locate bond functions, the question of superposition error is present.

In order to better understand the results of PB and to assess if the apparent importance of the bond function outweighs the associated problems, a series of calculations were performed on $C\ell O$ and the $C\ell$ atom.

Computational Details

Our double zeta (DZ) basis sets are constructed as follows: Dunning's[2] DZ contraction of the Huzinga[3] primitive set is used for oxygen (9s5p/4s2p), and Dunning's[4] DZ contraction of the Veillard[5] primitive set is used for Chlorine (12s9p/6s4p). PB's basis set is slightly different for $C\ell$, using Veillard's[5] contraction instead of Dunning's.[4] This difference is small and we chose Dunning's contraction because it has some additional flexability in the valence region. The DZ plus polarization (DZP) basis set starts from the

DZ basis and adds atomic centered d polarization functions to both O
and Cℓ. The value of the exponent is that of PB; $\alpha(Cℓ) = 0.50211$ and
$\alpha(O) = 0.537333$. The bond functions were located at the bond midpoint
and the exponents are those of PB; $\alpha(s) = 0.6$, $\alpha(p) = 0.7$ and
$\alpha(d) = 0.5188$. The notation we use to describe the addition of bond
functions is; +Bf (list of functions added). For example a DZ basis
with the addition of s and p bond functions would be denoted,
DZ + Bf(sp). The DZ plus two sets of polarization functions (DZ2P)
basis set starts with the same primitive sets, but contracts them in a
more flexibile manner, O(9s5p/5s3p) and Cℓ(12s9p/7s5p), then adds 2 sets
of atomic d functions; $\alpha(O) = 1.85$ and 0.55, and $\alpha(Cℓ) = 1.48$ and 0.44.

Three additional basis sets were used. DZP' uses the same DZ basis
sets as DZP, but uses different d exponents, $\alpha(O) = 0.75$ and $\alpha(Cℓ) = 0.60$.
Two general contractions[6] of the primitive sets of DZP' were used;
G1 O(9s5p1d/3s2p1d) and Cℓ(12s9p1d/4s3p1d) and G2 O(9s5p1d/4s3p1d)
and Cℓ(12s9p1d/5s4p1d).

All calculations were performed using MOLECULE - noname[7] , except
those involving general contractions which used BIGGMOLI[8]- noname.

CℓO has a $^2\Pi$ ground state with occupation,

$$1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad 6\sigma^2 \quad 7\sigma^2 \quad 1\pi^4 \quad 2\pi^4 \quad 3\pi^3. \tag{1}$$

We ran a 2 configuration MCSCF including configuration (1) and a second
important configuration which is needed to dissociate to natural Cℓ and
O,

$$1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad 6\sigma^2 \quad 8\sigma^2 \quad 1\pi^4 \quad 2\pi^4 \quad 3\pi^3. \tag{2}$$

Using the orbitals obtained from this MCSCF, we performed a first order[9]
CI (FOCI) calculation. The 1-6σ and 1Π were held fully occupied.
This corresponds to the Cℓ 1s, 2s, 2p, and 3s and the O 1s and 2s.

At infinite separation we treated the system in a different manner.
We optimized the orbitals using a single SCF configuration,

$$1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad 6\sigma^2 \quad 7\sigma \quad 8\sigma \quad 1\pi^4 \quad 2\pi^4 \quad 3\pi^3 \quad {}^4\Pi. \quad (3)$$

We also performed the FOCI as a ${}^4\Pi$ state.

The calculation of the superposition error for Cℓ was as follows.
A single-configuration SCF was used to optimize the orbitals. The configu-
ration used was

$$1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^1 \quad 1\pi^4 \quad 2\pi^4 \quad {}^2\Sigma^+ . \quad (4)$$

Two CI calculations were performed, both included all single and double
excitations from configuration (4). The first correlated only the 3p
electrons, CI(3p). The second correlated both the 3s and 3p electrons,
CI (3s3p). Both CI calculations used a cumulative - A_K selection (this
procedure is described in references 10 and 11) and the interacting space.[12]
The magnitude of coefficient of (4) in the CI wavefunction is $\sim$.97.
Therefore a K of 1 was employed in the selection process. For the DZP
basis we ran tests with thresholds of 1×10^{-5} and 3×10^{-5}. This is an
ideal case for selection, the perturbation estimate corresponds very closely
to the computed difference. Most calculations use a threshold of 1.0×10^{-5}
except DZ2P, DZP', G1 and G2 which use a threshold of 3.0×10^{-5}. Based
on our tests we estimate that our CI results are accurate to at least

1.0×10^{-4}. These calculations were performed for $C\ell$ with only the $C\ell$ atomic centered function, then repeated with the oxygen centered and bond functions at the FOCI equilibrium bond length.

Results and Discussion

In Table I we have summarized the results of PB using bond functions, along with the results of Arnold, et al.[13] using a Slater basis and the experimental determination of Coxon, et al.[14] The DZ + Bf(sp) and DZP + Bf(spd) results of PB agree very well with the large STO basis calculation of Arnold and the experimental result.

In Table II we have summarized the results of our FOCI on $C\ell O$ and the superposition error for the SCF and both levels of CI. The first thing to note is that all atomic centered basis sets give approximately the same superposition error, while the inclusion of bond functions increases the SCF superposition error only a small amount, but greatly increases the CI superposition error. The effect is most pronounced when the $C\ell$ 3s is correlated.

PB results show a large (0.48 eV) increase in D_e when a bond centered d function is added to the DZP + Bf(sp) basis set. The same change in basis has a very small (0.05 eV) effect on our FOCI results, but shows a very large (0.15 eV) increase in the CI superposition error for $C\ell$. Similarly, the DZ + Bf(sp) results which are much better than one would expect, show a very large CI superposition error.

The apparaent success of PB with bond functions seems to rely on a cancellation of errors, the increase in CI superposition error which cancels the errors associated with a finite basis and limited CI expansion. While these errors appear to cancel for $C\ell O$ and N_2, it does not seem safe

to assume they will cancel in general. It therefore seems reasonable to conclude that the bond functions must be used with great caution.

We would like to note some less extensive tests on CI superposition error. The DZP', G1 and G2 were all run with the oxygen basis placed at the DZP FOCI equilibrium bond length. The DZP' results show that using more common d exponents rather than the atom optimized d functions increases the CI superposition error only slightly. Also the superposition error error associated with the general contractions is essentially the same as with DZP basis sets.

Conclusions

The CI superposition associated with basis sets containing bond function is shown to be very large. When atomic center d functions are also included the CI superposition is reduced, but can still be very large. For $C\ell$ with a DZP + Bf(spd) the CI(3s3p)/SD superposition error is 0.41 eV, or 15% of the dissociation error. It is concluded that bond functions should be avoided and atomic centered polarization functions used.

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Table I.

Previous CℓO Results

Basis	D_e (eV)	R_e (bohr)
DZ + Bf(sp)[a]	2.69	
DZP + Bf(sp)[a]	2.28	
DZP + Bf(spd)[a]	2.76	
STO[6]	2.75	3.06
Exp[G]	2.803 ± 0.001	2.966

a   ref 1.

b   ref 12.

c   ref 13.

Table II.

Summary of FOCI Results for ClO and Superposition Error for the Cl Atom.

| | ClO | | Cl | | |
| | | | Superposition Error (eV) | | |
	R_e	D_e(eV)	SCF	CI(3p)	CI(3s3p)
DZ	3.46	1.12	0.004	0.022	0.087
DZ + Bf(sp)	3.15	2.15	0.013	0.259	0.702
DZP	3.09	2.24	0.008	0.041	0.087
DZP + Bf(sp)	3.08	2.40	0.022	0.101	0.256
DZP + Bf(spd)	3.08	2.45	0.025	0.155	0.408
DZ2P	3.03	2.52	0.012	0.049	0.103
DZP'	3.09[a]		0.007	0.056	0.092
G1	3.09[a]		0.007	0.059	0.097
G2	3.09[a]		0.006	0.055	0.092

[a] DZP equilibrium bond length used.